# **Supporting Information**

# Experimental

# 1. Synthesis of Protic salts based on N,N-Dimethylethylenediamine cation

1) 1-(N,N-Dimethylamino)-2-(ammonium)ethane triflate ([DMEDAH][Tf]) - Neat Sample

The compound was made by a proton transfer reaction between 1 mole of triflic acid and 1 mole of N,N-dimethylethylenediamine. Typically the synthesis involves a dropwise addition of aqueous solution of triflic acid (42 mmoles, 6.3g) to N,N-dimethylethylenediamine (42 mmoles, 3.7g) in an ice bath and the contents were stirred for about 2 hours at room temperature. Then water was removed by distillation and the final solid product was dried under vacuum at 70  $^{\circ}$  C for two days and the yield was found to be 98 %. The pH of a 0.1 M aqueous solution of the product was found to be 8.0.

## 2) [DMEDAH][Tf] with 5mol% acid doped sample

The 5 mol % triflic acid doped sample was made by weighing 2.26 g (95 mol%) of neat [DMEDAH][Tf] and added 0.075 g (5 mol%) of aqueous solution of triflic acid to it. The contents were stirred to get clear liquid and then distilled at 70  $^{\circ}$  C to remove water under reduced pressure. The solid was dried under vacuum for two days at room temperature and the yield was found to be 98 %..

## 3) [DMEDAH][Tf] with 10mol% acid doped sample

The 10 mol% acid doped sample was made by mixing 2.14 g (90 mol%) of neat [DMEDAH][Tf] with 0.15 g (10 mol%) of aqueous solution of triflic acid and the contents were stirred to get clear liquid. The liquid was then distilled at 70  $^{\circ}$  C to remove water under reduced pressure. The solid was dried under vacuum for two days at room temperature and the yield was found to be 98 %.

# 4)1-(N,N-Dimethylammonium)-2-(ammonium)ethane-triflate ([DMEDAH<sub>2</sub>][Tf]<sub>2</sub>) – Neat Sample

The title compound was made by the proton transfer reaction between 2 moles of triflic acid and 1 mole of N,N-dimethylethylenediamine. The synthesis involves a drop wise addition of aqueous solution of triflic acid (84 mmoles, 12.5g) to N,N-dimethylethylenediamine (42 mmoles, 3.7g) in an ice bath and the contents were stirred for about 2 hours at room temperature. Then water was removed by distillation and the final solid product was dried under vacuum at 70  $^{0}$  C for two days and the yield was found to be 98 %. The pH of a 0.1 M aqueous solution of the product was found to be 2.1.

## 5) [DMEDAH<sub>2</sub>][Tf]<sub>2</sub> with 5mol% acid doped sample

The 5 mol % triflic acid doped sample was made by stirring 2.27 g of N,N-Dimethylethane-1,2-diammonium triflate with 0.075 g of aqueous solution of triflic acid to get clear liquid. The contents were then distilled at 70  $^{\circ}$  C to remove water under reduced pressure. The solid is dried under vacuum for two days at room temperature and the yield was found to be 98 %.

# 2. Differential scanning calorimetry (DSC)

In this work DSC is performed on a Mettler Toledo DSC instrument. All samples were prepared and seal in the glove box under argon atmosphere. In order to obtain accurate data, a calibration using cyclohexane reference was carried out. A temperature range of  $-100^{\circ}$ C to  $200^{\circ}$ C and scan rate of  $10^{\circ}$ C/min was used to study the thermal behavior of the materials. Three temperature scans were run and the first scan was often different to the other two due to the thermal history thus the second scan was reported.

## 3. Electrochemical impedance spectroscopy (EIS)

Ionic conductivity is measured by electrochemical impedance. All the samples were dried under vacuum on a schlenk line below their melting points. A pair of platinum electrodes was used. Pellets were prepared by pressing the samples in a sealed KBR die under 10 tons pressure. For the soft samples which can be pressed out or extensively deformed under compression, a dip cell was used to measure their ionic conductivity. The dip cell consists of two platinum electrodes covered by glass and dipped into the sample in liquid state. Preparation of samples in the dip cell was performed in the glove box and the impedance measurement was started after sealing the dip cell under argon atmosphere.

A Bio-logic SP-200 potentiostat driven by Solartron Modulab MTS System was used for the barrel cell EIS measurements. A tubular Helios furnace (28V, 32W) with a flexible ceramic heater was used to control the temperature. The heaters were controlled by a Eurotherm 2204e or 3501e temperature controller interfaced to the potentiostats, allowing impedance spectra to be acquired automatically throughout a programmed isothermal temperature profile. An amplitude of 0.1V and frequency range of 1 MHz – 1 Hz was applied over a temperature range of  $25^{\circ}C \sim 70^{\circ}C$ .

For dip cell measurements, Biologic MTZ - 35 Analyser was used to obtain the conductivity. The dip cell was placed in a brass block connected to a Eurotherm 2204 temperature controller. Liquid nitrogen or dry ice pellets were used to decrease temperature below the room temperature. Data was collected over a frequency range from 10 MHZ to 100 mHZ with a voltage amplitude of 0.1 V and over a temperature range of -25°C to 50°C at 5°C intervals.

All the samples were held at the target temperature for an equilibration time of 30min before impedance measurements.

## 4. Solid-static NMR

The solid-state experiments in this project were performed on a Bruker Avance III 300 MHz wide bore NMR spectrometer with Larmor frequency of 300.13 MHz, 75.46MHz for 1H and 13C respectively. All 1H and 13C chemical shifts were referenced relative to tetramethylsilane (TMS). A 4 mm double resonance Magic Angle Spinning (MAS) probe head was used to record the spectra from stationary

powder samples. For all experiments, the 90° pulse lengths were 2.0  $\mu s$ , and the recycle delays were 10s to allow the system to recover to equilibrium. The sample temperatures for the variable temperature experiments were calibrated with lead nitrate.

## <sup>1</sup>H and <sup>19</sup>F diffusion coefficient measurements

The samples were sealed in a 4mm solid-state NMR rotor and then was put in a standard 5mm glass tubes for measurement. <sup>1</sup>H and <sup>19</sup>F NMR tests were carried on a Bruker Avance III 300MHz wide bore NMR spectrometer with a 5mm diff50 pulse-field gradient probe. The <sup>1</sup>H and <sup>19</sup>F NMR signals of all the samples were used for the determination of the diffusion coefficients of the cation and anion groups respectively.

## Supporting data



Fig. S1  $^{13}\text{C}$  CPMAS NMR spectra obtained from [DMEDAH][Tf] and [DMEDAH\_2][Tf]\_2 at 20°C with the peak assignment shown on the molecular structures

<sup>13</sup>C CPMAS spectra from [DMEDAH][Tf] and [DMEDAH<sub>2</sub>][Tf]<sub>2</sub> at 20°C are shown in Fig. S1. The spectra show good resolution and the peaks are assigned to various molecular sites as shown in their molecular structure. As can be seen from the spectra, the NMR shifts for two –CH3 groups are identical in [DMEDAH<sub>2</sub>][Tf]<sub>2</sub>, which suggest the cation structure is more symmetric than that of [DMEDAH][Tf].



**Fig. S2** Simulated <sup>13</sup>C CPMAS NMR shifts and structures of the cations in [DMEDAH][Tf] (b) and  $[DMEDAH_2][Tf]_2$  (c) at 20°C

<sup>13</sup>C NMR chemical shifts in the cations of [DMEDAH][Tf] and [DMEDAH<sub>2</sub>][Tf]<sub>2</sub> at 20°C were calculated using density functional theory (DFT) method, and the calculated values were compared with the experimental results. The order of the predicted NMR shifts for four cation-carbons is consistent with the shifts in experimental NMR spectra. It is clear that the overlapped peaks of C2 and C3 sites, belonging to two methyl groups in [DMEDAH<sub>2</sub>][Tf]<sub>2</sub>, become split in [DMEDAH][Tf]. This suggests that the cation structure is more symmetric in [DMEDAH<sub>2</sub>][Tf]<sub>2</sub>, which explain the higher melting point of [DMEDAH<sub>2</sub>][Tf]<sub>2</sub>



[DMEDAH<sub>2</sub>][Tf]<sub>2</sub>

Fig. S3 compares the <sup>1</sup>H and <sup>19</sup>F NMR spectra of the pure [DMEDAH][Tf] and  $[DMEDAH_2][Tf]_2$  measured at different temperature. All the spectra show progressive line-narrowing with increasing temperature indicating increasing molecular dynamics. As we can see from the <sup>1</sup>H NMR spectra, in all the temperatures selected, there are more narrow peaks occurring in [DMEDAH\_2][Tf]\_2, which means more diffusive cation exists. The behaviour of the static spectra for <sup>19</sup>F is similar to that of the <sup>1</sup>H.





Fig. S7 <sup>13</sup>C solution NMR spectrum of [DMEDAH<sub>2</sub>][Tf]<sub>2</sub>

The <sup>13</sup>C solution NMR spectra of [DMEDAH][Tf] and [DMEDAH<sub>2</sub>][Tf]<sub>2</sub> are shown in Fig. S5 and Fig. S7 respectively. The chemical shift assignments confirmed the molecular structure of the synthesized samples. In the DEPT-135 spectra (Fig. S6) CH<sub>2</sub> groups show negative charge whereas CH<sub>3</sub> groups have positive peak which further confirmed our assignment.

## Reference

1. Zheng, W.; Mohammed, A.; Hines Jr, L. G.; Xiao, D.; Martinez, O. J.; Bartsch, R. A.; Simon, S. L.; Russina, O.; Triolo, A.; Quitevis, E. L., Effect of cation symmetry on the morphology and physicochemical properties of imidazolium ionic liquids. *The Journal of Physical Chemistry B* **2011**, *115* (20), 6572-6584.